CLAIMS

WHAT IS CLAIMED IS:

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- 1. A process for preparing haloalkanes which comprises:
 - a) mixing and heating carbon tetrachloride with an olefin in a reactor in the
 presence of metallic iron, dissolved iron species, and an organophosphate cocatalyst to produce a continuous flow of reactor effluent containing a
 haloalkane product,
 - b) treating the reactor effluent from step a) with a solid-liquid separation device that separates coarse solid iron particles from the liquid and returns the course solid iron particles to the reactor, to produce by this separation a reactor effluent containing a decreased concentration of coarse solid iron particles,
 - c) distilling the reactor effluent from step b) in a catalyst recovery unit to produce a continuous flow of overhead product containing an increased concentration of product haloalkane and a continuous flow of bottom product containing increased concentrations of dissolved iron and phosphoruscontaining species that are active in the catalysis of the reaction to make product haloalkane, and
 - d) recycling a portion of the bottom product from step c) to the reactor while purging the rest from the system.

2. The process of claim 1 wherein the organophosphate co-catalyst is trialkylphosphate.

3. The process of claim 2 wherein the trialkylphosphate co-catalyst is tributylphosphate or tripropylphosphate or triisobutylphosphate.

- 4. The process of claim 1 wherein the main inputs to the reactor are: carbon tetrachloride, ethene, tributylphosphate, metallic iron, and recycle catalyst from the catalyst recovery unit, and the product haloalkane is 1,1,1,3-tetrachloropropane.
 - 5. The process of claim 1 wherein the solid-liquid separation device is a centrifuge, a hydrocyclone, a filter or a sedimentation tube.
 - 6. A process for preparing haloalkane which comprises:
 - a) mixing and heating carbon tetrachloride with an olefin in a reactor in the presence of metallic iron, dissolved iron species, and an organophosphate cocatalyst to produce a continuous flow of reactor effluent containing product haloalkane, and
 - b) treating the reactor effluent from step a) with a solid-liquid separation device that separates coarse solid iron particles from the liquid and returns them to the reactor, to produce a reactor effluent containing a decreased concentration of coarse particles, and
 - c) distilling the reactor effluent from step b) in a catalyst recovery unit to produce a continuous flow of overhead product containing an increased concentration of product haloalkane and a continuous flow of bottom product

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containing increased concentrations of dissolved iron and phosphoruscontaining species which are active in the catalysis of the reaction to make product haloalkane, and

d) distilling the bottom product from step c) in a continuous or batch secondary catalyst recovery unit to produce an overhead product containing an increased concentration of product haloalkane and a bottom product containing a increased concentrations of dissolved iron and phosphorus-containing components that are active in the catalysis of the reaction to make product haloalkane, and

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- e) recycling a portion of the bottom product from step d) to the reactor while purging the rest from the system.
- 7. The process of claim 6 wherein the organophosphate co-catalyst is trialkylphosphate.
- 8. The process of claim 7 wherein the trialkylphosphate co-catalyst is tributylphosphate or tripropylphosphate or triisobutylphosphate.
- 9. The processes of claim 6 wherein the main inputs to the reactor are: carbon tetrachloride, ethene, tributylphosphate, metallic iron, and recycle catalyst from the catalyst recovery unit, and the product haloalkane is 1,1,1,3-tetrachloropropane.
 - 10. The process of claim 6 wherein the solid-liquid separation device is a centrifuge, a hydrocyclone, a filter, and a sedimentation tube.

11. A method of producing a haloalkane comprising reacting ethene, carbon tetrachloride, tributylphosphate, and iron in a reactor to produce a reaction effluent, separating the reaction effluent by distillation into an overhead fraction of desired haloalkane, ethene and carbon tetrachloride and a bottom fraction of catalyst components for return to the reactor, in the distillation step of the effluent, the overhead containing 1,1,1,3-tetrachloropropane as well as ethene and carbon tetrachloride.

- 12. In the process of claim 11 wherein the ethene and carbon tetrachloride are separated by distillation and returned to the reactor.
- 13. In the process of claim 11 wherein the bottoms fraction, which contains 1,1,1,3-tetra-chloropropane, 1,1,1,5-tetrachloropentane and higher molecular weight compounds, is subjected to distillation at a temperature of 70 to 115° C and at a pressure of 40 to 225 torr to obtain the purified 1,1,1,3-tetrachloropropane.
- 14. The process of claim 13 wherein the distillation temperature is 80 to 105° C and the pressure is 62 to 160 torr.
 - 15. The process of claim 14 wherein the distillation temperature is 93° C and the pressure is 103 torr.
 - 16. The process of claim 13 wherein the bottoms fraction is returned to the reactor after removal of the 1,1,1,3-tetrachloropropane.

17. The process of claim 11 wherein the bottom fraction is subjected to a second distillation at a temperature of 70 - 115° C after the first distillation at 70 - 115° C in order to produce an increased concentration of 1,1,1,3-tetrachloropropane and the residue of the distillation containing catalyst components may be recycled to the reactor.

- 5 18. The process of claim 11 wherein the reaction in the reactor is carried out at below 150° C.
 - 19. The process of claim 18 wherein the process is carried out at below 130° C.
 - 20. The process of claim 19 wherein the reaction time in the reactor is between 0.2 and 20 hours.
- 21. In the process of claim 11, the liquid residence time is 0.2 to 20 hours; the temperature is $90 130^{\circ}$ C and the pressure is 30 200 psig.
 - 22. A method for preparing 1,1,1,3-tetrachloropropane comprising the steps of
 - a) reacting ethene with carbon tetrachloride, in the presence of a metallic iron
 and ferric chloride catalyst and a tributylphosphate co-catalyst.
- b) separating the solids from the liquid reaction mixture,
 - c) distilling the liquid reaction mixture at a temperature of from 70 to 115° C, and at pressure of from 40 to 225 torr overhead pressure, to produce an overhead fraction rich in 1,1,1,3-tetrachloropropane and a bottom fraction

containing catalyst components, 1,1,1,3-tetrachloropropane, and unwanted high-boiling byproducts.

d) distilling the bottom fraction a second time at a temperature of 70 to 115° C and at 40 to 225 torr to obtain additional 1,1,1,3-tetrachloropropane.